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November 25, 1925

Sir:-

I have the honor to transmit herewith  
the annual report of the Fixed Nitrogen Research  
Laboratory for the fiscal year ending June 30, 1925.

Respectfully,

F. G. Cottrell  
Director

The Honorable,

The Secretary of Agriculture.

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ANNUAL REPORT OF THE DIRECTOR OF THE FIXED NITROGEN RESEARCH

LABORATORY FOR FISCAL YEAR ENDING JUNE 30, 1925.

P. 1

INTRODUCTION

This is the sixth year of operation of the Laboratory and its fourth year under the Department of Agriculture.

The downward trend in the price of synthetic ammonia is rapidly making its introduction into agriculture possible. This reduction is not only a desirable but necessary step in the transition from high priced ammonia, which could be afforded only for such uses as the chemical and refrigerative ones, into agricultural use, which requires the lower cost. For example, in Germany the agricultural use of synthetic ammonia on a large scale has been brought about as a result of post-war readjustments. The prospect is gratifying that the agricultural interests in the United States will also be able to enjoy the benefits of synthetic ammonia as a fertilizer material through regular commercial development in the course of peace-time operations.

The work of the year has been marked by the increase in direct service which the Laboratory has been able to render to the nitrogen fixation and allied industries. The work has reached such a stage that the results of the past years of research can be applied on a commercial scale. Through cooperation with a company engaged in the production of ammonia, the Laboratory has had a comprehensive group of its developments in synthetic ammonia put into continuous operation on a full sized commercial scale. It has been gratifying that this equipment has demonstrated its effectiveness.

THE DIRECT SYNTHETIC AMMONIA PROCESS

This process continues to appear the most favorable for the economic production of ammonia under present conditions. While the tonnage that is being produced in the U.S. is still but a small fraction of our national requirements, there has been a great increase in the interest in its possibilities and several new companies have either entered the field or are making plans to do so. On account of this active commercial interest, the Laboratory has become a center for consultation and advice, and has also furnished a number of trained men directly to the industry. The commercial plant mentioned in the last Annual Report has been completed and is in successful operation. Another similar plant also based on the Laboratory plans is already under construction.

There are many indications that the synthetic ammonia industry in the U.S. is rapidly passing through its initial stages and that its growth will soon be accelerated into large tonnages.

THE PRODUCTION OF HYDROGEN

The cost of suitable hydrogen still remains the largest item (about half) of the cost of synthesizing ammonia. The two most promising sources of cheap hydrogen appeared to be water-gas and coke oven gas. A general impression has been current that the latter is in large part either wasted or used for purposes where less valuable fuels could be substituted in this country and has hitherto not been utilized for ammonia production. A careful survey was therefore made of its possibilities under the varying industrial conditions. The amount of coke oven gas actually wasted was found to be only





2% of the total, but even so, enough is sometimes wasted at a single plant to furnish 20 tons of ammonia per day. The amount of coke oven gas used under boilers is about 4% of the total produced and has an average value of about 6.5¢ per thousand cubic feet. With gas at 10¢ per thousand it appears that coke oven gas might still in some cases compete with water-gas as a source of hydrogen, though water-gas seems clearly indicated as the dominant source for really large scale production. The method of separation by refrigeration and liquefaction, both with or without the use of solid or liquid absorbents, deserves further detailed study and experimentation.

Another factor that will stimulate the production of synthetic ammonia is the fact that by-product hydrogen (in some cases electrolytic of high purity) is being wasted or used for boiler heating at several chemical plants in quantities up to 1 or 2 million cubic feet per day. It will generally be an economy for these plants to produce ammonia and the Laboratory is encouraging and assisting them in the undertaking.

### THE AMMONIA CATALYST

During the year the Catalyst and its method of manufacture as worked out by the Laboratory have been in successful use on a commercial scale. The Laboratory is continuing the study of factors that contribute to activity and length of life of the catalyst mechanically, chemically, and especially in its resistance to deterioration from impurities in the gases. Systematic attack on these problems is yielding good results.

The purely empirical method of improving the catalyst seems to have about reached its limit. Any further advances are much more to be expected from a fundamental attack on the underlying principles of contact catalysis. This has been begun in a number of directions and is yielding encouraging results and noted below.

### OTHER METHODS OF FIXING NITROGEN

#### Aluminum Alloy Nitride Process.

As possibly having an application at Muscle Shoals a method of fixing nitrogen in the form of ammonia has been carefully investigated and found quite worth considering in such a general survey of the situation as is now being conducted by the Muscle Shoals Inquiry. This method consists in first producing an aluminum silicon iron alloy in the electric furnace; then nitrifying and subsequently hydrolyzing in much the same way and with the same apparatus as used in the cyanamide process. However, serious economic limitations make it highly improbable that this method could ever furnish a complete solution of the problem there presented. Metallic aluminum would be a concomitant product of the cycle as a whole, and as its value would represent some 4 or 5 times that of the ammonia the latter must be considered the by-product. Even if the alloy can be made from low-grade bauxite containing also oxides of iron, silicon and titanium, such as are found near Muscle Shoals, the yields would presumably be poorer and the power consumption higher than for the higher grade ores and it thus becomes a question whether the difference in cost and availability would justify their use. Of course, in any case the hope of making an economic success of this process would be in carrying it out on a large scale. Through the cooperation of one of the in-





dustrial alloy companies opportunity has been secured to try out the reduction on a car-load scale. After the alloy is obtained no difficulties are encountered in nitrifying the aluminum with the aid of chlorides and fluorides of the alkali and alkaline earth metals as catalysts, and in hydrolyzing to obtain ammonia and sodium aluminate from which latter pure alumina can be separated and finally reduced electrically to metallic aluminum.

#### Cyanide Method.

Continuing work along this line the equilibria involved in the formation of sodium cyanide have been studied. The use of a molten bath of sodium carbonate with carbon in the manufacture of sodium cyanide gives some promise and is being further investigated particularly as to the best method of operation. The cooperation with the Bureau of Mines on cyanide found in blast furnaces has been continued. Work was completed on one commercial furnace and quantities of commercial significance were demonstrated by five large scale tests. It is planned to extend the work to another furnace in the near future.

#### THE BACTERIAL FIXATION OF NITROGEN

During the year this work has chiefly centered on a study of what the legume bacteria get from the plant in exchange for the nitrogen which they help it to secure from the atmosphere, and whether or to what extent artificial culture media may be made to take the place of the root nodules as a soil for these bacteria. While these bacteria will not thrive on any of the purely synthetic standard culture media of the bacteriologist it has been known that the addition of a little legume extract to such media causes a luxuriant growth. However, such plant extract is chemically so complex and carries so much fixed nitrogen as to completely obscure the mechanism of bacterial fixation that we wish to study. Efforts have therefore been directed toward determining just what constituent or constituents in the legume extract were necessary and sufficient as addition agents to the culture media. This has required long and patient investigation, the methods being much the same as those used for the isolation and study of vitamins, in that at the outset at least, only the physiological effects of the unknown constituents were available as guides in judging whether the chemical and physical processes employed were effecting any separations at all. While the active substances concerned have not yet been completely identified or separated in pure form, we have succeeded in concentrating them to a considerable extent into certain fractions of the material treated and determining some of their more important chemical properties. Their complete chemical identification and preparation in pure form now seems much more definitely in reach than at any previous time. It has also been found that certain non-legumes also yield extracts which are equally effective in stimulating growth of these bacteria. No positive evidence of nitrogen fixation has yet been secured in cultures outside the root nodules themselves, even when vigorous and luxuriant growth has been obtained. This makes the mechanism of the symbiotic relation between legume and bacteria all the more an important object of further study.



## METHODS OF NITROGEN CONVERSION

Since the various forms of fixed nitrogen are not equally suited for use as a fertilizer and for other purposes, the problems of converting one form into other more suitable forms have always demanded attention. At present the synthesis of urea from carbon dioxide and ammonia is being fully investigated. In Germany this process has been developed on a large industrial scale and urea has been directly introduced as a fertilizing material with good results. This conversion is especially advantageous in conjunction with a water-gas hydrogen plant from which the carbon dioxide is obtained as by-product otherwise useless. Installation of a small plant at the Laboratory is now being completed in order to work out its adaption to American conditions. Corrosion of the metal equipment by moist carbon dioxide and ammonia presents one of the greatest difficulties, and is reported to be still a very serious obstacle to the economic success even of the German plants. It presents a clear cut experimental problem in chemical engineering upon which the Laboratory is making a determined attack. It has been found that urea nitrate (a compound of one molecule of urea with one molecule of nitric acid) has explosive properties approaching those of T.N.T. and twice those of ammonium nitrate. Its cost should make it attractive as an explosive if no unfavorable properties are later disclosed. Its explosive properties have enlisted the interest of the Bureau of Mines and of the War Department.

The problem of oxidizing ammonia to nitric oxide and especially its subsequent oxidation, condensation, and conversion to concentrated nitric acid still leave wide room for improvement. Various possibilities, including the use of silica gel as an adsorbent and the direct combination under high pressure of nitrogen tetroxide, water and oxygen to form concentrated nitric acid are receiving intensive study and are yielding some encouraging results.

## GENERAL STUDY OF CATALYTIC PROCESSES

A broadly fundamental study of catalytic processes both in contact catalysis and in gases has been prosecuted vigorously in several directions during the past year.

X-ray examination of the catalysts themselves has afforded important information as to the distribution and condition function of the addition substances called "promoters".

The electrical properties of gaseous nitrogen have been further studied with a view to determining the nature of "active" nitrogen first described by Lewis in this country, and Strutt in England, and through this not only to ascertain whether it might open a direct way to nitrogen fixation but what may be still more important, give us a clearer and more fundamental grip on the inner nature and properties of this most important element. Indications from this study thus far are that this "active" state represents so high an energy content of the nitrogen molecules compared with that of typical commercial nitrogen compounds that it is highly unlikely it would be profitable to actually pass through such a stage in their production. On the other hand, the experiments hold out good promise of furnishing valuable information on the structure and properties of the nitrogen atom and molecule which will have real practical bearing on development of the other processes of nitrogen fixation.





The electrical behavior of the heated catalyst in a vacuum has proved of the greatest interest. It was discovered that our ammonia catalyst containing potassium as a promoter when heated in vacuum to say 900°C. becomes a strong source of positive potassium ions. Other alkali and alkaline earth metals used as promoters behave similarly to varying degrees, corresponding in a general way to what might be expected from their relative volatility and ionization potentials. This not only gives a new insight into the mechanism of catalysis but also furnishes a new and valuable source of positive ions, much richer and more controllable than any hitherto known.

#### RADIOACTIVE RESEARCHES WITH NITROGEN

In addition to the direct use of the electric current in the study of the fundamental properties and reactions of gaseous nitrogen, the rays for radioactive substances present certain experimental advantages. Work in this field has been undertaken through the loan of a considerable quantity of radium from the Department of the Interior. This work is undertaken not with the idea that it is likely in itself to offer a direct means of commercial synthesis or conversion, but that indirectly light will be thrown on the catalytic and activating processes, particularly through the study of the formation and decomposition of molecular "complexes" which are probably the intermediaries in all catalytic processes.

#### LIST OF PUBLICATIONS FROM THE FIXED

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(Chronologically arranged for fiscal year 1924-1925)

Deterioration of some Metals in Hot, Reducing Ammonia Gases.

Proc. Am. Soc. for Testing Materials, Vol. 24, Part II, 1924.

J. S. Vanick

Decomposition of Calcium Cyanamide on Storage.

Ind. & Eng. Chemistry, 16, #7, 684, July, 1924.

K. D. Jacob, H. J. Krase and J. M. Braham

Preparation of Guanidinium Salts from Calcium Cyanamide.

Ind. & Eng. Chemistry, 16, #8, 848, August, 1924.

J. S. Blair and J. M. Braham.

Nitrogen Survey - Trade Information Bulletin #270.

Part IV - The Nitrogen Situation in European Countries, Sept. 1924.

H. A. Curtis and F. A. Ernst.

Increasing Ammonia Production with Improved Catalysts.

Ind. & Eng. Chem., 16, #10, 1002, October, 1924.

A. T. Larson.

Trend of Developments in the Nitrogen Problem.

Ind. & Eng. Chem., 16, #12, 1277, December 1924.

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Chemical Changes Occurring in Calcium Cyanamide-Acid Phosphate Mixtures.  
Ind. & Eng. Chem., 17, #1, 64, January 1925.

K. D. Jacob and J. M. Braham.

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Chem. & Met. Eng., 32, #6, February 1925.

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The Norwegian Nitrate Industry,

Chem. & Met. Eng., 32, #8, February 1925.

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The Synthesis of Water over Nickel and Copper Catalysts.

J. Am. Chem. Soc., 47, #2, 346, February 1925.

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The Determination of Dicyanodiamide.

Ind. & Eng. Chem., 17, #3, 266, March 1925.

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Rapid Method for Determination of CO in Hydrogen.

Ind. & Eng. Chem., 17, #3, 317, March 1925.

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Toxicity Studies with Dicyanodiamide on Plants.

J. Agric. Research 30, #5, 419, March 1925.

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J. Amer. Chem. Soc., 47, 1015, April 1925.

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The Direct Synthesis of Ammonia; A Lecture Table Experiment.

J. Chemical Education 11, #4, April, 1925.

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The Determination of Cyanamide.

Ind. & Eng. Chem., 17, #5, 457, May 1925.

L. A. Pinck

Recovery of Nitrogen Oxides from Gas Mixtures by Adsorption on Silica Gel.

Ind. & Eng. Chem., 17, #6, 599, June 1925.

J. A. Almquist, V. L. Gaddy and J. M. Braham.



